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(54) MIXED REFRIGERANT FILLING METHOD, AND FILLED APPARATUS

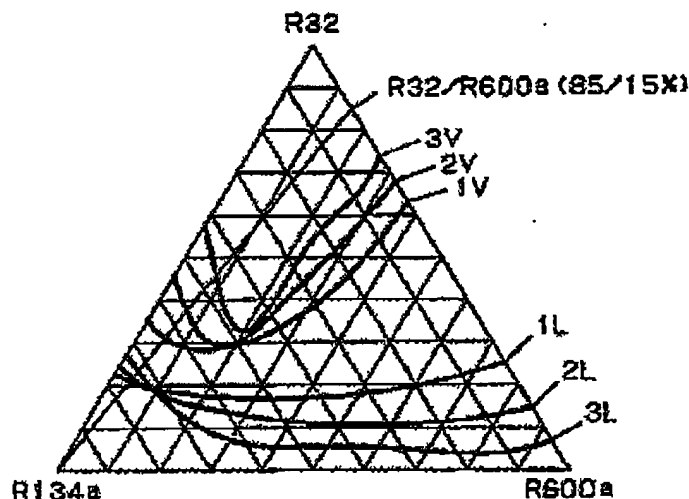
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**(54) Abstract**

**Purpose:** To provide a refrigerant filling method of a mixed refrigerant for replacing R22, R502, or R12, along with a filled apparatus.

**Solution means:** The present invention is a method that fills a mixed refrigerant composed of (a), (b), and (c), in which a mixed refrigerant consisting of a flammable hydrofluorocarbon refrigerant (a) and a nonflammable [sic; flammable] hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with the above-mentioned (a) and a nonflammable hydrofluorocarbon refrigerant (c), other than [different from] the above-mentioned (a), are not mixed in advance, in a refrigerant container. In forming a non-azeotropic mixed refrigerant containing a flammable hydrocarbon refrigerant, the composition change of the mixed refrigerant can be suppressed, and the mixed refrigerant can be simply and safely exchanged in various types of application.

**CLAIMS**

1. A mixed refrigerant filling method, characterized by the fact that a mixed refrigerant composed of a flammable hydrofluorocarbon refrigerant (a), a flammable hydrocarbon refrigerant (b), and a nonflammable hydrofluorocarbon refrigerant (c), in which a mixed refrigerant consisting of the flammable hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) used to form an azeotropic or azeotrope-like mixture with the above-mentioned hydrofluorocarbon refrigerant (a) mixed in advance, and in which the nonflammable hydrofluorocarbon refrigerant (c) other than the above-mentioned flammable hydrofluorocarbon refrigerant (a) are not mixed in advance, is filled in a refrigerant container.

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2. The mixed refrigerant filling method of Claim 1, characterized by the fact that the refrigerant container is a refrigeration cycle apparatus; with the mixed refrigerant composed of the hydrofluorocarbon refrigerant (a), the flammable hydrofluorocarbon (b), and the nonflammable hydrofluorocarbon refrigerant (c) being filled in the refrigerant container.

3. The mixed refrigerant filling method of Claim 1 or 2, characterized by the fact that the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the nonflammable hydrocarbon refrigerant (b) is a refrigerant with a low boiling point, and the nonflammable hydrofluorocarbon refrigerant (c) is a refrigerant with a high boiling point.

4. The mixed refrigerant filling method of Claim 1 or 2, characterized by the fact that the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the nonflammable hydrocarbon refrigerant (b) is a refrigerant with a high boiling point, and the nonflammable hydrofluorocarbon refrigerant (c) is a refrigerant with a low boiling point.

5. The mixed refrigerant filling method of Claim 1 or 2, characterized by the fact that the mixed refrigerant is composed of the hydrofluorocarbon refrigerant (a), the nonflammable hydrofluorocarbon refrigerant (c), and the nonflammable hydrocarbon refrigerant (b), in the order of a low boiling point.\*

6. The mixed refrigerant filling method of any of Claims 1-5, characterized by the fact that the hydrofluorocarbon refrigerant (a) is selected from difluoromethane (R32), pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a), 1,1,1,2-tetrafluoroethane (R134a), 1,1-difluoroethane (R152a), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2,2-pentafluoropropane (R245cb), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), and perfluoropropane (R218); the nonflammable hydrocarbon refrigerant (b) is selected from propane (R290), cyclopropane (RC270), isobutane (R600a), and butane (R600); and the nonflammable hydrofluorocarbon refrigerant (c), other than [different from] the above-mentioned hydrofluorocarbon refrigerant (a), is selected from pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), and perfluoropropane (R218).

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\* [Possibly meaning that the order (a), (c), (b) indicates substances with progressively lower boiling points.]

7. The mixed refrigerant filling method of Claim 6, characterized by the fact that the hydrofluorocarbon refrigerant (a) is difluoromethane (R32) or pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a) or 1,1,1,2-tetrafluoroethane (R134a), or 1,1-difluoroethane (R152a); the nonflammable hydrocarbon refrigerant (b) is isobutane (R600a) or butane (R600); and the nonflammable hydrofluorocarbon refrigerant (c), other than the above-mentioned hydrofluorocarbon refrigerant (a), is pentafluoroethane (R125) or 1,1,1,2-tetrafluoroethane (R134a).

8. The mixed refrigerant filling method of Claim 7, characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 80 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) along with 20 wt% or less of R600a or R600 as the nonflammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

9. The mixed refrigerant filling method of Claim 7, characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 90 wt% or more of R143a as the hydrofluorocarbon refrigerant (a) along with 10 wt% or less of R600a as the nonflammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

10. The mixed refrigerant filling method of Claim 7, characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 75 wt% or more of R134a as the hydrofluorocarbon refrigerant (a) along with 25 wt% or less of R600a or R600 as the nonflammable hydrocarbon refrigerant (b) and R125 as the nonflammable hydrofluorocarbon refrigerant (c).

11. The mixed refrigerant filling method of Claim 7, characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 70 wt% or more of R152a as the hydrofluorocarbon refrigerant (a) along with 30 wt% or less of R600a or R600 as the nonflammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

12. A refrigeration cycle apparatus, characterized by the fact that a mixed refrigerant is filled using the mixed refrigerant filling method of any of Claims 1-11.

## DETAILED EXPLANATION OF THE INVENTION

[0001]

### Technical field of the invention

The present invention pertains to a refrigerant filling method of a mixed refrigerant for replacing R22, R502, or R12, along with a filled apparatus.

[0002]

### Prior art

In various refrigeration cycle apparatuses such as air conditioners, refrigerators, and car air conditioners, a refrigeration cycle is constituted by connecting a compressor, if necessary, with throttle devices such as a four-way valve, condenser, capillary tube, and expansion valve, evaporator, etc., being connected via pipes; a refrigerant is filled and circulated in the refrigeration cycle apparatuses, so that a cooling action is realized. In these refrigeration cycle apparatuses, a hydrocarbon halide refrigerant derived from methane or ethane, called a flon<sup>\*</sup> refrigerant (hereinafter, described as ROO or ROOO) is usually used as a refrigerant.

[0003]

In particular, chlorodifluoromethane ( $\text{CHClF}_2$ , R22, boiling point of  $-40.8^\circ\text{C}$ , nonflammable) has been broadly used in air conditioners, freezers, etc., R502 (azeotropic refrigerant of chlorodifluoro methane R22 and chloropentafluoroethane R155, boiling point  $-45.3^\circ\text{C}$ , nonflammable) has been broadly used in freezers, refrigerators, etc., dichlorodifluoromethane ( $\text{CCl}_2\text{F}_2$ , R12, boiling point of  $-29.8^\circ\text{C}$ , nonflammable) has been broadly used in refrigerators, car air conditioners, etc., and trichlorofluoromethane ( $\text{CCl}_3\text{F}$ , R11, boiling point of  $23.7^\circ\text{C}$ , nonflammable) has been broadly used [in different devices].

[0004]

However, the ozone layer destruction of the stratosphere due to the flon refrigerant has recently become known as an environmental problem on a global scale, and since the flon refrigerant has a stratospheric ozone destruction capability, the regulation of the amount being used and the amount of flon refrigerant being produced has been determined by the Montreal International Agreement. Furthermore, there is a movement to discontinue its use and production in the future. In order to eliminate the influence on the stratospheric ozone layer, it is

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<sup>\*</sup> ["Flon" is a Japanese term whose Western equivalent (or near equivalent) is Freon.]

necessary to not include chlorine in the molecular structure, and a hydrofluorocarbon refrigerant containing no chlorine is proposed as a refrigerant suitable for the conditions of use.

[0005]

As examples of the hydrogen fluorocarbon catalyst containing no chlorine, there are difluoromethane ( $\text{CH}_2\text{F}_2$ , R32, boiling point of  $-51.7^\circ\text{C}$ , weakly flammable), pentafluoroethane ( $\text{CF}_3\text{-CHF}_2$ , R125, boiling point of  $-48.1^\circ\text{C}$ , nonflammable), 1,1,1-trifluoroethane ( $\text{CF}_3\text{-CF}_3$ , R143a, boiling point of  $-47.2^\circ\text{C}$ , weakly flammable), 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of  $-26.1^\circ\text{C}$ , nonflammable), 1,1-difluoroethane ( $\text{CHF}_2\text{-CH}_3$ , R152a, boiling point of  $-24.0^\circ\text{C}$ , weakly flammable), etc.

[0006]

Here, R134a is mostly used as an alternative refrigerant consisting of R12 in refrigerators, car air conditioners, etc., mixed refrigerants of R125/R143a/R134a, R125/R143a, etc., are proposed as alternative refrigerants of R502 in freezers, refrigerators, etc., and mixed refrigerants of R32/R125/R134a, R32/R125, etc., are proposed as alternative refrigerants of R22 in air conditioners, freezers, etc.

[0007]

#### Problems to be solved by the invention

However, in the above-mentioned hydrofluorocarbon refrigerant or the mixed refrigerant composed of a hydrofluorocarbon, the compatibility with a mineral oil or alkylbenzene oil that has been used as a conventional lubricant for compressors is poor, and the lubricant jetted with the refrigerant from the compressor is likely not to return to the compressor from a low-temperature evaporator. For this reason, in case the hydrofluorocarbon refrigerant or the mixed refrigerant composed of a hydrofluorocarbon is used as a refrigerant, it is also thought to be essential for the lubricant used for the compressor to be converted into a synthetic oil such as an ester oil or ether oil with good compatibility.

[0008]

Therefore, in various existing refrigeration cycle apparatuses such as air conditioners, freezers, refrigerators, and car air conditioners using refrigerants having a stratospheric ozone destruction capability, such as R22, R502, and R12, it is difficult to use the hydrofluorocarbon refrigerant or the mixed refrigerant composed of the hydrofluorocarbon.

[0009]

Also, in various existing refrigeration cycle apparatuses such as air conditioners, freezers, refrigerators, and car air conditioners using refrigerants having a stratospheric ozone destruction capability, such as R22, R502, and R12, not only are the operation temperature and the refrigeration performance different, but the setup of throttle devices such as a capillary tube and expansion valve used as constitutional elements of the refrigeration cycle apparatuses, the setup of the vapor pressure of additionally installed high-pressure switches and various kinds of safety devices, etc., have been established in accordance with the form of usage. Each time the refrigerant is exchanged [replaced] with an alternative refrigerant, its adjustment is required.

[0010]

For various existing refrigeration cycle apparatuses and refrigerant containers using refrigerants having such a stratospheric ozone destruction capability, the present invention provides a simple and safe method for replacing the refrigerants with alternative refrigerants, having no influence on the stratospheric ozone layer, and realizes an apparatus filled with said alternative refrigerants having no influence on the stratospheric ozone layer.

[0011]

In the present invention, utilizing the property in which a hydrocarbon refrigerant having no influence on a small amount of the stratospheric ozone layer and having good compatibility with a chemical structure close to that of a mineral oil or alkylbenzene oil to ensure return of the oil to a compressor of a conventional lubricant for compressors, the drawback of the hydrocarbon catalyst with a strong flammability is compensated by mixing a large amount of weakly flammable or nonflammable hydrofluorocarbon refrigerant.

[0012]

Also, in the present invention, when a strongly flammable hydrocarbon refrigerant is mixed with a weakly flammable or nonflammable hydrofluorocarbon refrigerant, a mixed refrigerant consisting of a hydrofluorocarbon refrigerant (a) with high azeotropy and a flammable hydrocarbon refrigerant (b) is used. The reason for this is that if the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) is a non-azeotropic mixture refrigerant, not only are the boiling temperature and the dew point temperature different, but the component with a low boiling point is easily concentrated in the gas phase and the component with a high boiling point is easily concentrated in the liquid phase, and the mixture composition ratio of a small amount of hydrocarbon refrigerant can greatly changed.

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[0013]

Furthermore, in consideration of different operation temperatures and levels of refrigeration performance, in the setup of throttle devices such as a capillary tube and expansion valve, the setup of the vapor pressure of high-pressure switches and various kinds of safety devices, etc., in order to select an appropriate alternative refrigerant, a mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) with high azeotropy and the flammable hydrocarbon refrigerant (b) is further mixed and adjusted.

[0014]

The mixed refrigerant consisting of the present invention is usually a non-azeotropic mixed refrigerant, and the composition change of the mixed refrigerant can be suppressed by filling the nonflammable hydrofluorocarbon refrigerant (c) first, then filling the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) with high azeotropy and the flammable hydrocarbon refrigerant (b), so that the mixture composition ratio of a small amount of hydrocarbon refrigerant can be completely filled without a large [composition] change.

[0015]

Thus, for various refrigeration cycle apparatuses using R22 and R502 for both an intermediate temperature and a low temperature, usually, two kinds of refrigerant containers - - a refrigerant container with a mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) having a boiling point lower than that of R22 and R502, and a refrigerant container with the nonflammable hydrofluorocarbon refrigerant (c) having a boiling point higher than that of R22 and R502 - - are prepared, and alternative refrigerants having no influence on the stratospheric ozone layer in various usages such as air conditioners, freezers, and refrigerators can be exchanged simply by filling while appropriately measuring them at an optional ratio.

[0016]

Also, for various refrigeration cycle apparatuses using R12 for both intermediate - - temperature and low-temperature operations, usually, two kinds of refrigerant containers - - i.e., a refrigerant container with a mixed refrigerant consisting of hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), with a boiling point lower than that of R12, and a refrigerant container with the nonflammable hydrofluorocarbon refrigerant (c), with a boiling point higher than that of R12, are prepared, and alternative refrigerants having no influence on the stratospheric ozone layer in various usages such as refrigerators and car air conditioners can

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be exchanged simply by filling while appropriately measuring [maintaining] them at an optional ratio.

[0017]

Furthermore, the filling method of the present invention pertains to a method for filling a non-azeotropic mixed refrigerant containing a strongly flammable hydrocarbon refrigerant; this filling method can be utilized for refrigerant containers by manufacturers as well as for service cans, when exchanging and repairing refrigeration cycle apparatuses and when repairing leaks.

[0018]

For the filling of a non-azeotropic three-component mixed refrigerant, a method that individually fills each component has also been considered, but as many facilities as the number of components in the individual filling are required, so that an enormous facility cost results. At the same time, not only is the filling work very complicated, but the concentration of the flammable refrigerant is raised in the non-azeotropic mixed refrigerant containing the strongly flammable hydrocarbon, so that there is a possibility of exhibiting flammability. However, according to the present invention, the refrigerants can always be filled with a constant [consistent] composition while always securing a safety operation.

[0019]

#### **Means to solve the problems**

In order to solve the above problems, the present invention provides a mixed refrigerant filling method characterized by the fact that that a mixed refrigerant composed of a flammable hydrofluorocarbon refrigerant (a), a flammable hydrocarbon refrigerant (b), and a nonflammable hydrofluorocarbon refrigerant (c), in which a mixed refrigerant consisting of the flammable hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with the above-mentioned hydrofluorocarbon refrigerant (a) mixed in advance, and in which the nonflammable hydrofluorocarbon refrigerant (c) other than the above-mentioned flammable hydrofluorocarbon refrigerant (a) are not mixed in advance, is filled in a refrigerant container.

[0020]

Also, the present invention is characterized by the fact that the refrigerant container is a refrigeration cycle apparatus, with the mixed refrigerant composed of the hydrofluorocarbon refrigerant (a), the flammable hydrofluorocarbon (b), and the nonflammable hydrofluorocarbon refrigerant (c) being filled in the refrigerant container.

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[0021]

Also, the present invention is characterized by the fact that the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the nonflammable hydrocarbon refrigerant (b) is a refrigerant with a low boiling point, and the nonflammable hydrofluorocarbon refrigerant (c) is a refrigerant with a high boiling point.

[0022]

Also, the present invention is characterized by the fact that the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the nonflammable hydrocarbon refrigerant (b) is a refrigerant with a high boiling point, and the nonflammable hydrofluorocarbon refrigerant (c) is a refrigerant with a low boiling point.

[0023]

Also, the present invention is characterized by the fact that the mixed refrigerant is composed of the hydrofluorocarbon refrigerant (a), the nonflammable hydrofluorocarbon refrigerant (c), and the nonflammable hydrocarbon refrigerant (b), in the order of low [progressively lower] boiling points.

[0024]

Also, the present invention is characterized by the fact that the hydrofluorocarbon refrigerant (a) is selected from difluoromethane (R32), pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a), 1,1,1,2-tetrafluoroethane (R134a), 1,1-difluoroethane (R152a), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2,2-pentafluoropropane (R245cb), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), and perfluoropropane (R218); the nonflammable hydrocarbon refrigerant (b) is selected from propane (R290), cyclopropane (RC270), isobutane (R600a), and butane (R600); and the nonflammable hydrofluorocarbon refrigerant (c), other than the above-mentioned hydrofluorocarbon refrigerant (a), is selected from pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), and perfluoropropane (R218).

[0025]

Also, the present invention is characterized by the fact that the hydrofluorocarbon refrigerant (a) is difluoromethane (R32) or pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a) or 1,1,1,2-tetrafluoroethane (R134a), or 1,1-difluoroethane (R152a); the nonflammable

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hydrocarbon refrigerant (b) is isobutane (R600a) or butane (R600); and the nonflammable hydrofluorocarbon refrigerant (c), other than the above-mentioned hydrofluorocarbon refrigerant (a), is pentafluoroethane (R125) or 1,1,1,2-tetrafluoroethane (R134a).

[0026]

Also, the present invention is characterized by the fact that the mixed refrigerant is composed of 80 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) along with 20 wt% or less of R600a or R600 as the nonflammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

[0027]

Also, the present invention is characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 90 wt% or more of R143a as the hydrofluorocarbon refrigerant (a) along with 10 wt% or less of R600a as the nonflammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

[0028]

Also, the present invention is characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 75 wt% or more of R134a as the hydrofluorocarbon refrigerant (a) along with 25 wt% or less R600a or R600 as the nonflammable hydrocarbon refrigerant (b) and R125 as the nonflammable hydrofluorocarbon refrigerant (c).

[0029]

Also, the present invention is characterized by the fact that the mixed refrigerant is composed of a mixed refrigerant consisting of 70 wt% or more R152a as the hydrofluorocarbon refrigerant (a) along with 30 wt% or less R600a or R600 as the nonflammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

[0030]

Also, the present invention provides a refrigeration cycle apparatus characterized by the fact that a mixed refrigerant composed of the hydrofluorocarbon refrigerant (a), the flammable hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with (a), and the nonflammable hydrofluorocarbon refrigerant (c), other than [different from] the above-mentioned (a).

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[0031]

**Embodiments of the invention**

Next, embodiments of the present invention are explained using the figures.

[0032]

**Embodiment 1**

It is necessary to select the combination of a mixed refrigerant composed of a hydrofluorocarbon refrigerant (a) with high azeotropy and a flammable hydrocarbon refrigerant (b) used in the mixed refrigerant filling method of the present invention from various kinds substances.

[0033]

As the flammable hydrocarbon refrigerant (b) having no influence on the stratospheric ozone layer, there are propane ( $\text{CH}_3\text{-CH}_2\text{-CH}_3$ , R290, boiling point of  $-42.1^\circ\text{C}$ , strongly flammable), cyclopropane ( $\text{C}_3\text{H}_6$ , RC270, boiling point of  $-32.9^\circ\text{C}$ , strongly flammable), isobutane ( $\text{i-C}_4\text{H}_{10}$ , R600a, boiling point of  $-11.7^\circ\text{C}$ , strongly flammable), butane ( $\text{n-C}_4\text{H}_{10}$ , R600, boiling point of  $-0.5^\circ\text{C}$ , strongly flammable), etc.

[0034]

In the combination of the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) having no influence on the stratospheric ozone layer and the flammable hydrocarbon refrigerant (b), as the hydrofluorocarbon refrigerant (a) for forming an azeotropic or an azeotrope-like mixture, there are difluoromethane ( $\text{CH}_2\text{F}_2$ , R32, boiling point of  $-51.7^\circ\text{C}$ , weakly flammable), pentafluoroethane ( $\text{CF}_3\text{-CHF}_2$ , R125, boiling point of  $-48.1^\circ\text{C}$ , nonflammable), 1,1,1-trifluoroethane ( $\text{CF}_3\text{-CH}_3$ , R143a, boiling point of  $-47.2^\circ\text{C}$ , weakly flammable), 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of  $-26.1^\circ\text{C}$ , nonflammable), 1,1-difluoroethane ( $\text{CHF}_2\text{-CH}_3$ , R152a, boiling point of  $-24.0^\circ\text{C}$ , weakly flammable), etc.

[0035]

In addition to these, in the combination of the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) having no influence on the stratospheric ozone layer and the flammable hydrocarbon refrigerant (b), as the hydrofluorocarbon refrigerant (a) for forming an azeotropic or an azeotrope-like mixture, there are 1,1,2,2-tetrafluoroethane ( $\text{CHF}_2\text{-CHF}_2$ , R134, boiling point of  $-19.8^\circ\text{C}$ , nonflammable), 1,1,1,2,2-pentafluoropropane ( $\text{CF}_3\text{-CF}_2\text{-CH}_3$ , R245cb, boiling point of  $-17.6^\circ\text{C}$ , weakly flammable), 1,1,1,2,3,3,3-heptafluoropropane ( $\text{CF}_3\text{-CHF-CF}_3$ ,

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R227ea, boiling point of  $-15.6^{\circ}\text{C}$ , nonflammable), 1,1,1,3,3,3-hexafluoropropane ( $\text{CF}_3\text{-CH}_2\text{-CF}_3$ , R236fa, boiling point of  $-1.4^{\circ}\text{C}$ , nonflammable), etc.

[0036]

Also, in the combination of the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) containing no hydrogen and the flammable hydrocarbon refrigerant (b), as the hydrofluorocarbon refrigerant (a) that forms an azeotropic or azeotrope-like mixture and that contains no hydrogen, there are perfluoropropane ( $\text{CF}_3\text{-CF}_2\text{-CF}_3$ , R218, boiling point of  $-36.8^{\circ}\text{C}$ , nonflammable), etc.

[0037]

In the mixed refrigerant consisting of said hydrofluorocarbon refrigerant (a) and flammable hydrocarbon refrigerant (b), as the combination for forming a main azeotropic or azeotrope-like mixture (outlined azeotropic composition), there are the following, but the combination used is not limited to them.

[0038]

- 1) R32/R290 (75/25 wt%), R32/RC270 (80/20 wt%), R32/R600a (85/15 wt%), and R32/R600 (90/10 wt%)
- 2) R125/R290 (90/10 wt%) and R125/RC270 (95/5 wt%)
- 3) R143a/R290 (75/25 wt%), R143a/RC270 (85/15 wt%), and R143a/R600a (95/5 wt%)
- 4) R134a/R290 (55/45 wt%), R134a/RC270 (65/35 wt%), R134a/R600a (80/20 wt%), and R134a/R600 (95/5 wt%)
- 5) R152a/R290 (40/60 wt%), R152a/RC270 (45/55 wt%), R152a/R600a (75/25 wt%), and R152a/R600 (85/15 wt%)

Also, in the above-mentioned combination for forming an azeotropic or azeotrope-like mixture, the combination in which the azeotropic composition of the hydrofluorocarbon refrigerant (a) is present at 70 wt% or more has a dew point temperature that is nearly the same as the boiling point temperature in a wide composition range from (azeotropic composition – 5 wt%) to less than 100%\* of the hydrofluorocarbon refrigerant (a), and the gas-phase composition and the liquid-phase composition are almost the same. It is apparent that a nearly azeotropic mixture that can be processed like a single refrigerant is formed.

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\* [Literal translation; possibly a phrase was omitted in the original document]

[0039]

For example, the following combinations can be mentioned.

[0040]

1) A mixed refrigerant consisting of 70 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) and 30 wt% or less of R290 as the flammable hydrocarbon refrigerant (b).

[0041]

2) A mixed refrigerant consisting of 75 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) and 25 wt% or less of RC270 as the flammable hydrocarbon refrigerant (b).

[0042]

3) A mixed refrigerant consisting of 80 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) and 25 wt% or less of R600a as the flammable hydrocarbon refrigerant (b).

[0043]

4) A mixed refrigerant consisting of 85 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) and 15 wt% or less of R600 as the flammable hydrocarbon refrigerant (b).

[0044]

5) A mixed refrigerant consisting of 85 wt% or more of R125 as the hydrofluorocarbon refrigerant (a) and 15 wt% or less of R290 as the flammable hydrocarbon refrigerant (b).

[0045]

6) A mixed refrigerant consisting of 90 wt% or more of R125 as the hydrofluorocarbon refrigerant (a) and 10 wt% or less of RC270 as the flammable hydrocarbon refrigerant (b).

[0046]

7) A mixed refrigerant consisting of 70 wt% or more of R143a as the hydrofluorocarbon refrigerant (a) and 30 wt% or less of R290 as the flammable hydrocarbon refrigerant (b).

[0047]

8) A mixed refrigerant consisting of 80 wt% or more of R143a as the hydrofluorocarbon refrigerant (a) and 20 wt% or less of RC270 as the flammable hydrocarbon refrigerant (b).

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[0048]

9) A mixed refrigerant consisting of 90 wt% or more of R143a as the hydrofluorocarbon refrigerant (a) and 10 wt% or less of R600a as the flammable hydrocarbon refrigerant (b).

[0049]

10) A mixed refrigerant consisting of 75 wt% or more of R134a as the hydrofluorocarbon refrigerant (a) and 25 wt% or less of R600a as the flammable hydrocarbon refrigerant (b).

[0050]

11) A mixed refrigerant consisting of 90 wt% or more of R134a as the hydrofluorocarbon refrigerant (a) and 10 wt% or less of R600 as the flammable hydrocarbon refrigerant (b).

[0051]

12) A mixed refrigerant consisting of 70 wt% or more of R152a as the hydrofluorocarbon refrigerant (a) and 30 wt% or less of R600a as the flammable hydrocarbon refrigerant (b).

[0052]

13) A mixed refrigerant consisting of 80 wt% or more of R152a as the hydrofluorocarbon refrigerant (a) and 20 wt% or less of R600 as the flammable hydrocarbon refrigerant (b).

[0053]

Also, in the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and a small amount of flammable hydrocarbon refrigerant (b), use can be made of any combination for forming an azeotropic or azeotrope-like mixture such that the azeotrope-like mixture has the lowest boiling point, with the boiling point being lower than that of each component, i.e., the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b).

[0054]

Here, the mixed refrigerant consisting of the hydrofluorocarbon refrigerant (a) and a small amount of flammable hydrocarbon refrigerant (b) is a weakly flammable or nonflammable mixture, but in order to use it as an alternative refrigerant consisting of various existing refrigeration cycle apparatuses, it is preferable to mix the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), and a nonflammable hydrofluorocarbon refrigerant other than the above-mentioned (a), to reduce the filling times to the extent possible.

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[0055]

For example, there are the following choices in using an alternative refrigerant with a vapor pressure nearly equivalent to that of R22, R502, and R12 as conventional refrigerants.

[0056]

A) A combination of the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the boiling point is lowered, and the nonflammable hydrofluorocarbon refrigerant (c) in which the boiling point is raised, other than the above-mentioned (a).

[0057]

B) A combination of the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the boiling point is raised, and the nonflammable hydrofluorocarbon refrigerant (c), in which the boiling point is lowered, other than the above-mentioned (a). Furthermore, it is very favorable for the flammable hydrocarbon refrigerant (b) for forming a nearly azeotrope-like mixture in a wide composition range and containing an azeotropic composition to be R600a or R600. In other words, since R600a or R600 has a boiling point close to that of a mineral oil and an alkylbenzene oil which are conventional lubricants for compressors, compared with other hydrocarbon refrigerants, the compatibility is greatly improved, and the formation of an azeotrope-like mixture in a wide composition range makes adjustment easy when it is mixed with a large amount of hydrofluorocarbon refrigerant.

[0058]

Also, if the flammable hydrocarbon refrigerant (b) is R600a or R600, since the boiling point is highest in almost all the cases, compared with the hydrofluorocarbon refrigerant (a) and the nonflammable hydrofluorocarbon refrigerant (c), the possibility that the flammable hydrocarbon refrigerant (b) will leak is lowest, and a safe filling operation can be realized.

[0059]

Therefore, as alternative refrigerants of R22 or R502 used in the method of the present invention, the following combinations are appropriate substances.

[0060]

As the combination (A) of the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the

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boiling point is lowered, and the nonflammable hydrofluorocarbon refrigerant (c) in which the boiling point is raised: 1) a substance composed of a mixed refrigerant consisting of 80 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) along with 20 wt% or less of R600a or R600 as the flammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

[0061]

2) A mixed refrigerant composed of 90 wt% or more of R143a as the hydrofluorocarbon refrigerant (a) along with 10 wt% or less of R600a as the flammable hydrocarbon refrigerant (b) and R125 or R134a as the nonflammable hydrofluorocarbon refrigerant (c).

[0062]

As the combination (B) of the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the boiling point is raised, and the nonflammable hydrofluorocarbon refrigerant (c) in which the boiling point is lowered, 3) a mixed refrigerant composed of 75 wt% or more of R134a as the hydrofluorocarbon refrigerant (a) along with 25 wt% or less of R600a or R600 as the flammable hydrocarbon refrigerant (b) and R125 as the nonflammable hydrofluorocarbon refrigerant (c).

[0063]

4) A mixed refrigerant composed of 70 wt% or more of R152a as the hydrofluorocarbon refrigerant (a) along with 30 wt% or less of R600a or R600 as the flammable hydrocarbon refrigerant (b) and R125 as the nonflammable hydrofluorocarbon refrigerant (c).

[0064]

Also, as alternative refrigerants of R12 that is used in the method of the present invention, the following combinations are appropriate substances.

[0065]

As the combination (A) of the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the boiling point is lowered, and the nonflammable hydrofluorocarbon refrigerant (c) in which the boiling point is raised, 5) a mixed refrigerant composed of 70 wt% or more of R152a as the hydrofluorocarbon refrigerant (a) along with 30 wt% or less R600a or R600 as the flammable hydrocarbon refrigerant (b) and R134a as the nonflammable hydrofluorocarbon refrigerant (c).

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[0066]

The above-mentioned examples are main representative examples constituting an alternative refrigerant with a vapor pressure nearly equivalent to that of R22, R502, and R12 as the conventional refrigerants, but the present invention is not limited to them. An alternative refrigerant consisting to R11 as a conventional refrigerant can also be used.

[0067]

Therefore, as the hydrofluorocarbon refrigerant (a), combinations selected from difluoromethane (R32), pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a), 1,1,1,2-tetrafluoroethane (R134a), 1,1-difluoroethane (R152a), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2,2-pentafluoropropane (R245cb), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), and perfluoropropane (R218) can be used; as the nonflammable hydrocarbon refrigerant (b), combinations selected from propane (R290), cyclopropane (RC270), isobutane (R600a), and butane (R600) can be used.

[0068]

As the nonflammable hydrofluorocarbon refrigerant (c), other than the above-mentioned hydrofluorocarbon refrigerant (a), combinations selected from pentafluoroethane (R125), 1,1,1,2-tetrafluoroethane (R134a), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), and perfluoropropane (R218) can be used.

[0069]

#### **Embodiment 2**

Next, an application example of a ternary mixed refrigerant prepared using the mixed refrigerant filling method of the present invention, and its detailed refrigerant filling method, are explained using a vapor pressure diagram. Here, as a ternary mixed refrigerant used as an alternative refrigerant consisting to R22, as the combination (A) of an azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the boiling point is lowered, and the nonflammable hydrofluorocarbon refrigerant (c) in which the boiling point is raised, an application example containing R32 is explained, but a similar refrigerant filling method can also be mentioned for other ternary mixed refrigerants.

[0070]

Figure 1 shows an equilibrium state at a temperature of 50°C, 0°C, and -50°C using a mixed refrigerant composed of a mixture of three components - - difluoromethane ( $\text{CH}_2\text{F}_2$ , R32, boiling point of -51.7°C, weakly flammable) as the hydrofluorocarbon refrigerant (a), isobutane ( $\text{i-C}_4\text{H}_{10}$ , R600a, boiling point of -11.7°C, strongly flammable) as the flammable hydrocarbon refrigerant (b), and 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of -26.1°C, nonflammable) - - and at the same pressure as that of R22 [represented] by a triangular coordinate.

[0071]

In this triangular coordinate, the boiling point is low [progressively lower] in the order of R32, R134a, and R600a; at each apex of the triangle, single substances are arranged in the order of R32, R134a, and R600a counterclockwise with the upper apex as the base point, and the composition ratio (weight ratio) of each component at a certain point on the coordinate plane is expressed by the ratio of the distance of [from] the point and each side of the triangle. Also, at that time, the distance of the point and the side of the triangle corresponds to the composition ratio of the substances at the apex of the triangular coordinate opposite to the [respective] side.

[0072]

In the phase equilibrium diagram of Figure 1, 1 is a gas-liquid equilibrium line of a mixture having the same pressure as that of R22 at a temperature of 50°C, 2 is a gas-liquid equilibrium line of the mixture having the same pressure as that of R22 at a temperature of 0°C, and 3 is a gas-liquid equilibrium line of the mixture having the same pressure as that of R22 at a temperature of -50°C. The upper lines 1V, 2V, and 3V of the gas-liquid equilibrium lines 1, 2, and 3 are saturated gas lines, and the lower lines 1L, 2L, and 3L of the gas-liquid equilibrium lines 1, 2, and 3 are saturated liquid lines. In the range enclosed by these two lines, a gas-liquid equilibrium state is formed, and about the same pressure as that of R22 is shown at each temperature.

[0073]

In the composition in the area between 1V and 1L of the gas-liquid equilibrium line, at the same pressure as that of R22, the gas phase is condensed at a temperature higher than 50°C and transformed to the liquid phase at a temperature lower than 50°C; also at the same pressure as that of R22, the liquid phase is evaporated at a temperature lower than 50°C and transformed to the gas phase at a temperature higher than 50°C. In the composition in the area between 2V and 2L of the gas-liquid equilibrium line, at the same pressure as that of R22, the gas phase is

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condensed at a temperature higher than 0°C and transformed to the liquid phase at a temperature lower than 0°C, and at the same pressure as that of R22, the liquid phase is evaporated at a temperature lower than 0°C and changed to the gas phase at a temperature higher than 0°C. In the composition in the area between 3V and 3L of the gas-liquid equilibrium line, at the same pressure as that of R22, the gas phase is condensed at a temperature higher than -50°C and transformed to the liquid phase at a temperature lower than -50°C, and at the same pressure as that of R22, the liquid phase is evaporated at a temperature lower than -50°C and transformed to the gas phase at a temperature higher than -50°C.

[0074]

In other words, in an apparatus using R22 for intermediate temperature [operation, with R22] having a condensation temperature of 50°C and an evaporation temperature 0°C, the composition in the area between 1V and 2L of the gas-liquid equilibrium line, where the area between 1V and 1L of the gas-liquid equilibrium line and the area between the 2V and 2L of the gas-liquid equilibrium line are overlapped, is suitable as an alternative refrigerant consisting to R22. Similarly, in an apparatus using R22 for a low temperature [operation, with R22] having a condensation temperature of 0°C and an evaporation temperature of -50°C, the composition in the area between 2V and 3L of the gas-liquid equilibrium line, where the area between 2V and 2L of the gas-liquid equilibrium line and the area between the 3V and 3L of the gas-liquid equilibrium line are overlapped, is suitable as an alternative refrigerant to R22.

[0075]

As seen from the phase equilibrium diagram of Figure 1, in the ternary mixed refrigerant composed of R32/R134a/R600a, although the composition suitable for an intermediate temperature operation and the composition suitable for a low temperature operation are partially overlapped, to set the vapor pressure to a nearly equivalent to that of R22, the selectable composition range is greatly extended [much broader] in the range suitable for a low temperature operation, compared with the range suitable for an intermediate temperature operation.

[0076]

From the example of Figure 1, the alternative range [sic; composition] wherein the ternary mixed refrigerant composed of R32/R134a/R600a has a vapor pressure nearly equivalent to that of R22 in both an intermediate temperature operation and a low temperature operation is a ternary system composed of 4-75 wt% R32, 0-77 wt% R134a, and 0-93 wt% R600a.

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[0077]

Here, in case difluoromethane ( $\text{CH}_2\text{F}_2$ , R32, boiling point of  $-51.7^\circ\text{C}$ , weakly flammable) as the hydrofluorocarbon refrigerant (a) and isobutane ( $i\text{-C}_4\text{H}_{10}$ , R600a, boiling point of  $-11.7^\circ\text{C}$ , strongly flammable) as the flammable hydrocarbon refrigerant (b) are used, an azeotropic or azeotrope-like mixture is formed using 80 wt% or more of R32 as the hydrofluorocarbon refrigerant (a) and 20 wt% or less of R600a as the flammable hydrocarbon refrigerant (b). In particular, for the composition composed of 85 wt% of R32 as the hydrofluorocarbon refrigerant (a) and 15 wt% of R600a as the flammable hydrocarbon refrigerant (b), the boiling point is lower than that of 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of  $-26.1^\circ\text{C}$ , nonflammable) used as the nonflammable hydrofluorocarbon refrigerant (c) as well as [that of] R32 and R600a of each component.

[0078]

Therefore, for example, a line that connects the composition composed of 85 wt% of R32 as the hydrofluorocarbon refrigerant (a) and 15 wt% of R600a as the flammable hydrocarbon refrigerant (b), being an azeotropic mixture, and with R134a as the nonflammable hydrofluorocarbon refrigerant (c) is drawn on the phase equilibrium diagram of Figure 1. In other words, two kinds of refrigerant containers - - that with the mixed refrigerant composed of 85 wt% R32 as the hydrofluorocarbon refrigerant (a) and 15 wt% R600a as the flammable hydrocarbon refrigerant (b), and a refrigerant container with approximately 45-75wt% R134a as the nonflammable hydrocarbon refrigerant (c) - - are prepared; R134a as the nonflammable hydrocarbon refrigerant (c) is filled in the refrigerant container with the mixed refrigerant composed of 85 wt% R32 as the hydrofluorocarbon refrigerant (a) and 15 wt% R600a as the flammable hydrocarbon refrigerant (b) while appropriately measuring [using these] at an optional ratio in a range of about 25-55 wt%.

[0079]

This corresponds to the fact that the line that connects the composition composed of 85 wt% R32 as the hydrofluorocarbon refrigerant (a) along with 15 wt% R600a as the flammable hydrocarbon refrigerant (b) and R134a as the nonflammable hydrofluorocarbon refrigerant (c) is appropriately internally divided and filled at an optional ratio on the phase equilibrium diagram of Figure 1. Therefore, if the line that connects the composition composed of 85 wt% R32 as the hydrofluorocarbon refrigerant (a) along with 15 wt% R600a as the flammable hydrocarbon refrigerant (b) and R134a as the nonflammable hydrofluorocarbon refrigerant (c) is appropriately internally divided and filled between 1V and 2L of the gas-liquid equilibrium line on the phase equilibrium diagram of Figure 1, an alternative refrigerant with a vapor pressure nearly

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equivalent to that of R22 can be exchanged in an apparatus using R22 for an intermediate temperature operation, and if the line is internally divided and filled between 2V and 3L of the gas-liquid equilibrium line, filled and an alternative refrigerant with a vapor pressure nearly equivalent to that of R22 can be exchanged in an apparatus using R22 for a low temperature operation.

[0080]

At that time, from the example of Figure 1, the range [system] wherein the ternary mixed refrigerant composed of R32/R134a/R600a has a vapor pressure nearly equivalent to that of R22 for both an intermediate temperature operation and a low temperature operation is a ternary system composed of about 20-45 wt% R32, about 45-75 wt% R134a, and about 3.5-8.5 wt% R600a.

[0081]

In the above-mentioned example of the filling method, an exchange example in which the vapor pressure is nearly equivalent to that of R22 has been shown; however, since the vapor pressure is almost proportional to the refrigeration performance, the refrigeration performance can also be nearly equivalent [to that of R22]. In establishing the setup of throttle devices such as a capillary tube and expansion valve as constitutional elements of a refrigeration cycle apparatus, for example, the composition may be internally divided and filled so that the density of the saturated liquid is nearly equivalent to the density of the condensation-temperature saturated liquid of R22.

[0082]

In this filling method, in practice, R134a as the nonflammable hydrofluorocarbon refrigerant (c) that is nonflammable and has a high boiling point is filled first; the composition composed of 85 wt% R32 as the hydrofluorocarbon refrigerant (a) and 15 wt% R600a as the flammable hydrocarbon refrigerant (b) that is weakly flammable and has a low boiling point is filled while monitoring the state of the apparatus.

[0083]

Furthermore, according to the filling method of the present invention, the ternary mixed refrigerant composed of R32/R134a/R600a is a non-azeotropic mixed refrigerant, but compared with the method that individually fills each component - - R32, R134a, and R600a - - the concentration of R600a with strong flammability, which should be used in a small amount is not

raised, the composition change of the mixed refrigerant can be suppressed, and a constant composition can always be filled while always securing a safety operation.

[0084]

Figure 2 shows an equilibrium state at a temperature of 50°C, 0°C, and -50°C of a mixed refrigerant composed of a mixture of three components - - difluoromethane ( $\text{CH}_2\text{F}_2$ , R32, boiling point of -51.7°C, weakly flammable) as the hydrofluorocarbon refrigerant (a), butane ( $\text{n-C}_4\text{H}_{10}$ , R600, boiling point of -0.5°C, strongly flammable) as the flammable hydrocarbon refrigerant (b), and 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of -26.1°C, nonflammable) - - and at the same pressure as that of R22, as represented by a triangular coordinate.

[0085]

From the example of Figure 2, the alternative range [system] wherein the ternary mixed refrigerant composed of R32/R134a/R600 has a vapor pressure nearly equivalent to that of R22 for both an intermediate temperature operation and a low temperature operation is a ternary system composed of 7-74 wt% R32, 0-77 wt% R134a, and 0-92 wt% R600a.

[0086]

Therefore, for example, a line that connects the composition composed of 90 wt% R32 as the hydrofluorocarbon refrigerant (a) and 10 wt% R600 as the flammable hydrocarbon refrigerant (b), being an azeotropic mixture, and R134a as the nonflammable hydrofluorocarbon refrigerant (c), is drawn on the phase equilibrium diagram of Figure 2. In other words, two kinds of refrigerant containers - - i.e., a refrigerant container with the mixed refrigerant composed of 90 wt% R32 as the hydrofluorocarbon refrigerant (a) and 10 wt% R600 as the flammable hydrocarbon refrigerant (b), and a refrigerant container with R134a as the nonflammable hydrocarbon refrigerant (c) - - are prepared; about 45-75 wt% R134a as the nonflammable hydrocarbon refrigerant (c) and about 25-55 wt% [of substances taken] from the refrigerant container of the mixed refrigerant composed of 90 wt% R32 as the hydrofluorocarbon refrigerant (a) and 10 wt% R600 as the flammable hydrocarbon refrigerant (b) are filled while appropriately measuring [using the substances] at an optional ratio.

[0087]

At that time, from the example of Figure 2, the range [system] wherein the ternary mixed refrigerant composed of R32/R134a/R600 has a vapor pressure nearly equivalent to that of R22 for both an intermediate temperature operation and a low temperature operation is a ternary

system composed of about 25-50 wt% R32, about 45-75 wt% R134a, and about 2.5-5.5 wt% R600a [sic; R600].

[0088]

Therefore, if the case wherein the alternative range [system] in which the vapor pressure is nearly equivalent to that of R22 is replaced with R32/R600 instead of R32/R600a is also considered, the ternary system composed of about 25-50 wt% R32, about 45-75 wt% R134a, and about 2.5-8.5 wt% R600a or R600 can be utilized as an alternative refrigerant consisting of R22 for both an intermediate-temperature and a low-temperature operation.

[0089]

(Table I) shows the comparison of an ideal refrigeration performance using a specific mixture composition of a ternary component composed of 85 wt%/15 wt% R32/R600a mixed refrigerant and R134a compared with that of R22 for an intermediate temperature operation. The conditions for an intermediate temperature operation are a condensation average temperature of 50°C, an evaporation average temperature of 0°C, a condenser-outlet supercooling degree of 0 deg, and an evaporator-outlet overheating degree of 0 deg.

[0090]

As seen from (Table I), for example, a ternary system composed of 30 wt% R32/R600a (85 wt%/15 wt%) and 70 wt% R134a, that is, a ternary system composed of 25.5 wt% R32, 70 wt% R134a, and 4.5 wt% R600a, is characterized by being able to be filled as an alternative refrigerant consisting of apparatuses in which the pressure is almost equal, although the refrigeration performance is slightly lower than that of R22, and apparatuses in which the jet temperature is lowered.

[0091]

Also, for example, a ternary system composed of 40 wt% R32/R600a (85 wt%/15 wt%) and 60 wt% R134a, that is, a ternary system composed of 34 wt% R32, 60 wt% R134a, and 6 wt% R600a, is characterized by being able to be filled as an alternative refrigerant consisting of apparatuses in which the refrigeration performance is raised, although the pressure is slightly higher than that of R22.

[0092]

In the example (Table I), the case wherein an azeotrope-like mixture refrigerant consisting containing 85 wt%/15 wt% R32/R600a is mixed at an optional ratio with a refrigerant

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having the high boiling point of R134a and filled as an alternative refrigerant consisting of an apparatus using R22 has been shown; however, optional vapor pressure and refrigeration performance can also be adjusted for the case where the azeotrope-like mixture refrigerant is filled as an alternative refrigerant consisting of an apparatus using R502.

[0093]

Also, the case in which R32/R600 is used as an alternative refrigerant instead of R32/R600a is similar, and in case the ternary system composed of about 20-50 wt% R32, about 45-75 wt% R134a, and about 2.5-8.5 wt% R600a or R600 is filled as an alternative refrigerant consisting of the apparatus using R22, the variable vapor pressure and refrigeration performance can be adjusted. For filling as an alternative refrigerant for various purposes in various apparatuses using R22 and R502, a ternary system composed of about 15-60 wt% R32, about 40-85 wt% R134a, and about 0-10 wt% R600a or R600 is preferable.

[0094]

(Table I)

Refrigerant	R22	(R32/600a(85/15))/R134a			
Composition ratio (wt%)	100	25/75	30/70	35/65	40/60
Refrigeration performance (compared with R22)	1.00	0.90	0.95	1.01	1.06
Coefficient of performance (compared with R22)	1.00	0.99	0.99	0.99	0.99
Condensation pressure (MPa)	1.95	1.88	1.98	2.08	2.18
Vapor pressure (MPa)	0.50	0.44	0.47	0.50	0.53
Jet temperature (°C)	74.4	67.1	68.8	70.4	71.7
Condensation temperature gradient (deg)	0.00	5.38	5.58	5.61	5.50
Evaporation temperature gradient (deg)	0.00	4.76	5.22	5.53	5.69

[0095]

### Embodiment 3

Also, an application example of a ternary mixed refrigerant prepared using the refrigerant filling method of the present invention, and its detailed refrigerant filling method, is explained using a vapor pressure diagram. Here, as a ternary mixed refrigerant used as an alternative refrigerant consisting of R22, as the combination (A) of an azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b), in which the boiling point is raised, and the nonflammable hydrofluorocarbon refrigerant (c) in which the boiling point is lowered, an application example containing R125 is explained; however, a similar refrigerant filling method can also be mentioned for other ternary mixed refrigerants.

[0096]

Figure 3 shows an equilibrium state at a temperature of 50°C, 0°C, and -50°C of a mixed refrigerant composed of a mixture of three components - - 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of -26.1°C, nonflammable) as the hydrofluorocarbon refrigerant (a), butane ( $\text{n-C}_4\text{H}_{10}$ , R600, boiling point of -0.5°C, strongly flammable) as the flammable hydrocarbon refrigerant (b), and pentafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R125, boiling point of -48.1°C, nonflammable) - - and at the same pressure as that of R22 [represented] by a triangular coordinate.

[0097]

In this triangular coordinate, the boiling is low in the order of R125, R134a, and R600, and at each apex of the triangle, single substances are arranged in the order of R125, R134a, and R600 counterclockwise near the upper apex as the base point, with the composition ratio (weight ratio) of each component at a certain point on the coordinate plane being expressed by the ratio of the distance of [from] the point and [to] each side of the triangle. Also, at that time, the distance of the point and the side of the triangle corresponds to the composition ratio of the substances at the apex of the triangular coordinate opposite to the [particular] side.

[0098]

In the phase equilibrium diagram of Figure 3, 1 is a gas-liquid equilibrium line of a mixture having the same pressure as that of R22 at a temperature of 50°C, 2 is a gas-liquid equilibrium line of the mixture having the same pressure as that of R22 at a temperature of 0°C, and 3 is a gas-liquid equilibrium line of the mixture having the same pressure as that of R22 at a temperature of -50°C. The upper lines 1V, 2V, and 3V of the gas-liquid equilibrium lines 1, 2, and 3 are saturated gas lines, and the lower lines 1L, 2L, and 3L of the gas-liquid equilibrium lines 1, 2, and 3 are saturated liquid lines. In the range enclosed with these two lines, a gas-liquid equilibrium state is formed, and about the same pressure as that of R22 is shown at each temperature.

[0099]

In the composition in the area between 1V and 1L of the gas-liquid equilibrium line, at the same pressure as that of R22, the gas phase is condensed at a temperature higher than 50°C and transformed to the liquid phase at a temperature lower than 50°C, and at the same pressure as that of R22, the liquid phase is evaporated at a temperature lower than 50°C and transformed to the gas phase at a temperature higher than 50°C. In the composition in the area between 2V and 2L of the gas-liquid equilibrium line, at the same pressure as that of R22, the gas phase is

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condensed at a temperature higher than 0°C and transformed to the liquid phase at a temperature lower than 0°C, and at the same pressure as that of R22, the liquid phase is evaporated at a temperature lower than 0°C and transformed to the gas phase at a temperature higher than 0°C. In the composition in the area between 3V and 3L of the gas-liquid equilibrium line, at the same pressure as that of R22, the gas phase is condensed at a temperature higher than -50°C and transformed to the liquid phase at a temperature lower than -50°C, and at the same pressure as that of R22, the liquid phase is evaporated at a temperature lower than -50°C and transformed to the gas phase at a temperature higher than -50°C.

[0100]

In other words, in an apparatus using R22 for an intermediate temperature [operation, with R22] having a condensation temperature of 50°C and an evaporation temperature 0°C, the composition in the area between 1V and 2L of the gas-liquid equilibrium line, where the area between 1V and 1L of the gas-liquid equilibrium line and the area between the 2V and 2L of the gas-liquid equilibrium line are overlapped, is suitable as an alternative refrigerant to R22. Similarly, in an apparatus using R22 for a low temperature operation having a condensation temperature of 0°C and an evaporation temperature -50°C, the composition in the area between 2V and 3L of the gas-liquid equilibrium line where the area between 2V and 2L of the gas-liquid equilibrium line and the area between the 3V and 3L of the gas-liquid equilibrium line are overlapped is suitable for an alternative refrigerant to R22.

[0101]

As seen from the phase equilibrium diagram of Figure 3, in the ternary mixed refrigerant composed of R125/R134a/R600, although the composition suitable for an intermediate temperature operation and the composition suitable for a low temperature operation are partially overlapped to set the vapor pressure to one nearly equivalent to that of R22, the selectable composition range is greatly extended in the range [choice of systems] suitable for a low temperature, compared with the range suitable for an intermediate temperature.

[0102]

From the example of Figure 3, the alternative range wherein the ternary mixed refrigerant composed of R125/R134a/R600 has a vapor pressure nearly equivalent to that of R22 for both an intermediate-temperature and a low-temperature operation is a ternary system composed of 57-97 wt% R125, 0-43 wt% R134a, and 0-39 wt% R600a.

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[0103]

Here, in case 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of  $-26.1^\circ\text{C}$ , nonflammable) as the hydrofluorocarbon refrigerant (a) and butane ( $\text{n-C}_4\text{H}_{10}$ , R600, boiling point of  $-0.5^\circ\text{C}$ , strongly flammable) as the flammable hydrocarbon refrigerant (b) are used, an azeotropic or azeotrope-like mixture is formed using 90 wt% or more R134a as the hydrofluorocarbon refrigerant (a) and 10 wt% or less R600 as the flammable hydrocarbon refrigerant (b). In particular, the composition composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) and 5 wt% R600 as the flammable hydrocarbon refrigerant (b), and the boiling point is lower than that of pentafluoroethane ( $\text{CF}_3\text{-CHF}_2$ , R125, boiling point of  $-48.1^\circ\text{C}$ , nonflammable) used as the nonflammable hydrofluorocarbon refrigerant (c), although the boiling point is lower than that of R134a and R600 of each component.

[0104]

Therefore, for example, a line that connects the composition composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) along with 5 wt% R600 as the flammable hydrocarbon refrigerant (b), being an azeotropic mixture, and R125 as the nonflammable hydrofluorocarbon refrigerant (c) is drawn on the phase equilibrium diagram of Figure 3. In other words, two kinds of refrigerant containers - - i.e., a refrigerant container with the mixed refrigerant composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) along with 5 wt% R600 as the flammable hydrocarbon refrigerant (b) and a refrigerant container of R125 as the nonflammable hydrocarbon refrigerant (c) are prepared; R125 used as the nonflammable hydrocarbon refrigerant (c) is filled in the refrigerant container with the approximately 20-40wt% mixed refrigerant composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) and 5 wt% R600 as the flammable hydrocarbon refrigerant (b) while appropriately measuring [these] at an optional ratio in a range of about 60-80 wt%.

[0105]

This corresponds to the fact that the line that connects the composition composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) along with 5 wt% R600 as the flammable hydrocarbon refrigerant (b) and R125 as the nonflammable hydrofluorocarbon refrigerant (c) is appropriately internally divided and filled at an optional ratio on the phase equilibrium diagram of Figure 3. Therefore, if the line that connects the composition composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) along with 5 wt% R600 as the flammable hydrocarbon refrigerant (b) and R125 as the nonflammable hydrofluorocarbon refrigerant (c), is appropriately internally divided and filled between 1V and 2L of the gas-liquid equilibrium line on the phase equilibrium diagram of Figure 1, an alternative refrigerant with a vapor pressure nearly

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equivalent to that of R22 can be exchanged in an apparatus using R22 in an intermediate temperature operation, and if the line is internally divided between 2V and 3L of the gas-liquid equilibrium line and filled, an alternative refrigerant with a vapor pressure nearly equivalent to that of R22 can be exchanged in an apparatus using R22 in a low temperature operation.

[0106]

At that time, from the example of Figure 3, the range [system] wherein the ternary mixed refrigerant composed of R125/R134a/R600a has a vapor pressure nearly equivalent to that of R22 at both an intermediate temperature and a low temperature is a ternary system composed of about 60-80 wt% R125, about 20-40 wt% R134a, and about 1-2 wt% R600.

[0107]

In the above-mentioned example of the filling method, an example of exchange in which the vapor pressure [of the system] is nearly equivalent to that of R22 has been shown; however, since the vapor pressure is almost proportional to the refrigeration performance, the refrigeration performance can also be nearly equivalent [to that of R22]. In fitting to the setup of throttle devices such as a capillary tube and expansion valve as constitutional elements of a refrigeration cycle apparatus, for example, the composition may be internally divided and filled so that the density of the saturated liquid may be nearly equivalent to the density of the condensation-temperature saturated liquid of R22.

[0108]

In this filling method, in practice, R125 as the nonflammable hydrofluorocarbon refrigerant (c) that is nonflammable and has a high boiling point is filled first, and the composition composed of 95 wt% R134a as the hydrofluorocarbon refrigerant (a) and 5 wt% R600 as the flammable hydrocarbon refrigerant (b) that is nonflammable and has a low boiling point is filled while monitoring the state of the apparatus.

[0109]

Furthermore, according to the filling method of the present invention, the ternary mixed refrigerant composed of R125/R134a/R600 is a non-azeotropic mixed refrigerant; however, compared with the method that individually fills each component of R125, R134a, and R600, the concentration of R600 with strong flammability, which should be used in a small amount, is not raised, the composition change of the mixed refrigerant can be suppressed, and a constant composition can always be filled while always securing a safe operation.

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[0110]

Figure 4 shows an equilibrium state at a temperature of 50°C, 0°C, and -50°C of a mixed refrigerant composed of a mixture of three components - - 1,1,1,2-tetrafluoroethane ( $\text{CF}_3\text{-CH}_2\text{F}$ , R134a, boiling point of -26.1°C, nonflammable) as the hydrofluorocarbon refrigerant (a), isobutane ( $\text{i-C}_4\text{H}_{10}$ , R600a, boiling point of -11.7°C, strongly flammable) as the flammable hydrocarbon refrigerant (b), and pentafluoroethane ( $\text{CF}_3\text{-CHF}_2$ , R125, boiling point of -48.1°C, nonflammable) - - and at the same pressure as that of R22 [represented] by a triangular coordinate.

[0111]

From the example of Figure 4, the alternative range [system] wherein the ternary mixed refrigerant composed of R125/R134a/R600a has a vapor pressure nearly equivalent to that of R22 in both an intermediate-temperature and a low-temperature operation is a ternary system composed of 52-91 wt% R125, 0-43 wt% R134a, and 0-45 wt% R600a.

[0112]

Therefore, for example, a line that connects the composition composed of 80 wt% R134a as the hydrofluorocarbon refrigerant (a) along with 20 wt% R600a as the flammable hydrocarbon refrigerant (b), being an azeotropic mixture, and R125 as the nonflammable hydrofluorocarbon refrigerant (c) is drawn on the phase equilibrium diagram of Figure 4. In other words, two kinds of refrigerant containers - - refrigerant container with the mixed refrigerant composed of 80 wt% R134a as the hydrofluorocarbon refrigerant (a) along with 20 wt% R600a as the flammable hydrocarbon refrigerant (b) and a refrigerant container of R125 as the nonflammable hydrocarbon refrigerant (c) - - are prepared, and about 55-75 wt% R125 as the nonflammable hydrocarbon refrigerant (c) and about 25-45 wt% [of the substance] from the refrigerant container with the mixed refrigerant composed of 80 wt% R134a as the hydrofluorocarbon refrigerant (a) and 20 wt% R600a as the flammable hydrocarbon refrigerant (b) are filled while appropriately measuring at an optional ratio.

[0113]

At that time, from the example of Figure 4, the range [system] wherein the ternary mixed refrigerant composed of R125/R134a/R600a has a vapor pressure nearly equivalent to that of R22 in both an intermediate-temperature and a low-temperature operation is a ternary system composed of about 55-75 wt% R125, about 20-40 wt% R134a, and about 5-9 wt% R600a.

[0114]

Therefore, if the system wherein the vapor pressure is nearly equivalent to that of R22 is replaced with R125/R600a instead of R125/R600 is also considered, the ternary system composed of about 55-80 wt% R125, about 20-40 wt% R134a, and about 1-9 wt% R600a or R600 can be utilized as an alternative refrigerant to R22 for both an intermediate-temperature and a low-temperature operation.

[0115]

(Table II) shows the comparison of an ideal refrigeration performance with a specific mixture composition of a ternary component composed of 95 wt%/5 wt% R134a/R600 mixed refrigerant and R125 compared with that of R502 for an intermediate temperature operation. The conditions for an intermediate temperature operation are a condensation average temperature of 50°C, an evaporation average temperature of 0°C, a condenser-outlet supercooling degree of 0 deg, and an evaporator-outlet overheating degree of 0 deg.

[0116]

As seen from (Table II), for example, a ternary system composed of 40 wt% R134a/R600 (95 wt%/5 wt%) and 60 wt% R125, that is, a ternary system composed of 60 wt% R125, 38 wt% R134a, and 2 wt% R600 is characterized by being able to be filled as an alternative refrigerant in apparatuses in which the pressure and the jet [jetting of liquid or gas] temperature are lowered, although the refrigeration performance is slightly lower than that of R502.

[0117]

Also, for example, a ternary system composed of 30 wt% R134a/R600 (95 wt%/5 wt%) and 70 wt% R125, that is, a ternary system composed of 70 wt% R125, 28.5 wt% R134a, and 1.5 wt% R600, is characterized by being able to be filled as an alternative refrigerant consisting of apparatuses in which the refrigeration performance, lower than that of R502, is slightly improved and the jet temperature is lowered by setting the pressure to a value near that of R502.

[0118]

In the example (Table II), the case wherein an azeotrope-like mixture refrigerant consisting of 95 wt%/5 wt% R134a/R600 is mixed at an optional ratio in a refrigerant with the high boiling point of R134a and filled as an alternative refrigerant consisting of an apparatus using R502 has been shown; however, optional vapor pressure and refrigeration performance levels can be adjusted for the case wherein the azeotrope-like mixture refrigerant is filled as an alternative refrigerant consisting of an apparatus using R22.

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[0119]

Also, the case wherein R134a/R600a is used as an alternative refrigerant instead of R134a/R600 is similar, and in case the ternary system composed of about 55-80 wt% R125, about 20-40 wt% R134a, and about 1-9 wt% R600a or R600 is filled as an alternative refrigerant consisting of the apparatus using R502, optional vapor pressure and refrigeration performance levels can be adjusted. For filling as an alternative refrigerant for various purposes in various apparatuses using R22 and R502, a ternary system composed of about 50-85 wt% R125, about 15-50 wt% R134a, and about 0-10 wt% R600a or R600 is preferable.

[0120]

(Table II)

Refrigerant	R502	R134a/600(95/5)/R125			
Composition ratio (wt%)	100	25/75	30/70	35/65	40/60
Refrigeration performance (compared with R502)	1.00	0.88	0.88	0.85	0.83
Coefficient of performance (compared with R502)	1.00	0.92	0.94	0.95	0.96
Condensation pressure (MPa)	2.09	2.10	2.03	1.96	1.89
Vapor pressure (MPa)	0.57	0.52	0.50	0.48	0.46
Jet temperature (°C)	59.4	55.0	55.1	55.2	55.3
Condensation temperature gradient (deg)	0.02	2.20	2.48	2.69	2.83
Evaporation temperature gradient (deg)	0.00	2.09	2.29	2.41	2.48

[0121]

**Embodiment 4**

Also, an application example of the ternary mixed refrigerant filling method of the present invention is explained using an application example of Figure 5. In Figure 5, 11 is a high-boiling-point refrigerant container sealed with R134a as the nonflammable hydrofluorocarbon refrigerant (c), 12 is a measurer for a high-boiling-point refrigerant, 13 is an azeotrope-like-mixture refrigerant container with a R32/R600a mixed refrigerant composed of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with the hydrofluorocarbon refrigerant (a), and 14 is a measurer for an azeotrope-like mixed refrigerant. An azeotrope-like mixed refrigerant with a boiling point lower than that of the high-boiling-point substance 11 is inserted into an azeotrope-like-mixture refrigerant container 13. Also, a vacuum device 15 and valves for an opening and closing operation along with them are connected to another pipe system 17 having a refrigerant filling port 16.

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[0122]

Here, in a refrigeration cycle apparatus 20, compressor 21, four-way valve 22, condenser 23, throttle device 24 such as a capillary tube and expansion valve, evaporator 25, etc., are connected by pipes, with R22 as a conventional refrigerant, mineral oil, alkylbenzene oil, or a mixed oil being sealed in the compressor 21. Also, the four-way valve 22 is not required for apparatuses such as freezers and refrigerators that carry out only a simple cooling action. In this case, the vacuum device 15 also shares a refrigerant injection port 26 and a connecting pipe 27 installed in a low-pressure line between the evaporator 25 of the refrigeration cycle apparatus 20 and the suction port of the compressor 21, and the refrigerant filling port 16 for exhaust and releases the gas under vacuum. A ternary mixed refrigerant is then filled from refrigerant injection port 26 in the order of: a refrigerant with a high boiling point from the high-boiling-point refrigerant container 11 and an azeotrope-like mixture refrigerant with a lower boiling point from the azeotrope-like mixture refrigerant container 13 at [in relation to] a prescribed amount of refrigerant in the refrigeration cycle apparatus 20 while measuring the amount. In this manner, R22 as a conventional refrigerant is exchanged with R32/R134a/R600a as an alternative refrigerant having no influence on the stratospheric ozone layer.

[0123]

Therefore, after the refrigerant with a high boiling point measured is filled from the high-boiling-point refrigerant container 11, the azeotrope-like mixture refrigerant being filled from the azeotrope-like mixed refrigerator container 13 can be processed like a single refrigerant since the boiling point temperature and the dew point temperature are almost the same, and the gas-phase composition and the liquid-phase composition are also almost the same. A strongly flammable hydrocarbon refrigerant that is included in the azeotrope-like mixture refrigerant is not filled at more than the desired composition [level] in the refrigeration cycle apparatus 20, regardless of the liquid filling and gas filling, and an appropriate amount of desired ternary composition can be filled.

[0124]

At that time, since the nonflammable hydrofluorocarbon refrigerant (c) as a refrigerant with a high boiling point is filled first, the pressure in the refrigeration cycle apparatus 20 is not greatly raised, and the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) as a refrigerant with a low boiling point can be filled. In case the azeotrope-like mixture refrigerant is filled while operating the refrigeration cycle apparatus 20, since the pressure of the low-pressure line of the refrigeration cycle apparatus 20 is lowered, the refrigerant can be more easily filled. Here, needless to say,

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the azeotrope-like mixture refrigerant consisting of the hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) may also be a refrigerant with a high boiling point, and the nonflammable hydrofluorocarbon refrigerant (c) may also be a refrigerant with a low boiling point.

[0125]

Also, in the application example of Figure 5, a vacuum process using the vacuum device 15, a high-boiling-point refrigerant filling measuring process using the high-boiling-point refrigerant container 11, and an azeotrope-like mixture refrigerant filling measuring work from the azeotrope-like mixture refrigerant container 13, in that order, are carried out at the installation site of the refrigeration cycle apparatus 20 while reconnecting the connecting pipe 27 with the refrigerant injection port 26; however, needless to say, a ternary mixture refrigerant filling apparatus in which the high-boiling-point refrigerant container 11, measurer 12 for a high-boiling-point refrigerant, azeotrope-like mixture refrigerant container 13, measurer 14 for an azeotrope-like mixed refrigerant, vacuum device 15, and refrigerant filling port 16 are connected by one pipe system 17.

[0126]

In the refrigeration cycle apparatus filled with the non-azeotropic mixture refrigerant composed of the hydrofluorocarbon refrigerant (a), flammable hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with the hydrofluorocarbon refrigerant (a), and the nonflammable hydrofluorocarbon refrigerant (c) other than the above-mentioned hydrofluorocarbon refrigerant (a) in this manner, conventional refrigerants such as R22, R502, and R12 having a stratospheric ozone layer destruction capability are exchanged with alternative refrigerants having no influence on the stratospheric ozone layer by a simple and safe method. Also, the exchange of a mineral oil and an alkylbenzene oil, the setup of throttle devices such as a capillary tube and expansion valve, the setup of the vapor pressure of an additionally arranged high-pressure switch and various kinds of safety devices, etc., are not required.

[0127]

In the explanation of the above-mentioned application examples, R134a has been used as a refrigerant with a high boiling point, and the R32/R600a mixed refrigerant, which is an azeotrope-like mixed refrigerant, has been used as a refrigerant with a low boiling point. However, the present invention is not necessarily limited to the combination of these three components. For example, ternary mixed refrigerants such as R32/R600 and R134a, R143a/R600a and R134a, R134a/R600a and R125, R134a/R600 and R125, R152a/R600a and

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R125, and R152a/R600 and R125 as alternative refrigerants to R22 and R502, and R152a/R600a and R134a and R152a/R600 and R134a as alternative refrigerants to R12, may also be used.

[0128]

**Effects of the invention**

As seen from the above explanation, the present invention pertains to the method that fills a mixed refrigerant composed of the flammable hydrofluorocarbon refrigerant (a), the flammable hydrocarbon refrigerant (b), and the nonflammable hydrofluorocarbon refrigerant (c), in which a mixed refrigerant consisting of the flammable hydrofluorocarbon refrigerant (a) and the flammable hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with the hydrofluorocarbon refrigerant (a) mixed in advance, and in which the nonflammable hydrofluorocarbon refrigerant (c) other than the above-mentioned flammable hydrofluorocarbon refrigerant (a), are not mixed in advance, in a refrigerant container. Also, the present invention pertains to a device such as a refrigeration cycle apparatus filled with a mixed refrigerant composed of the hydrofluorocarbon refrigerant (a), the flammable hydrocarbon refrigerant (b) for forming an azeotropic or azeotrope-like mixture with the hydrofluorocarbon refrigerant (a), and the nonflammable hydrofluorocarbon refrigerant (c) other than the above-mentioned flammable hydrofluorocarbon refrigerant (a). In various existing refrigeration cycle apparatuses with different operation temperatures and refrigeration performance levels such as air conditioners, freezers, refrigerators, and car air conditioners using conventional refrigerants such as R22, R502, and R12 having a stratospheric ozone layer destruction capability, a mineral oil, and an alkylbenzene oil, the filling ratio of an azeotrope-like mixture refrigerant containing a nonflammable hydrofluorocarbon refrigerant and a strongly flammable hydrocarbon refrigerant is set to an optional level, so that the conventional refrigerants can be exchanged with an alternative refrigerant having no influence on the stratospheric ozone layer by a simple and safe method, without changing the setup of throttle devices such as a capillary tube and expansion valve, the setup of the vapor pressure of an additionally arranged high-pressure switch and various kinds of safety devices, etc. In this method, a mixed refrigerant containing a strongly flammable hydrocarbon refrigerant is filled. Accordingly, the present invention can be utilized for filling into refrigerant containers by refrigerant manufacturers as well as for filling service cans, when exchanging and repairing refrigeration cycle apparatuses and in case of leaks.

## BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a triangular coordinate diagram showing an equilibrium state of a mixed refrigerant composed of a mixture of three components - - as a R32/R134a/R600a mixed refrigerant.

Figure 2 is a triangular coordinate diagram showing an equilibrium state of a mixed refrigerant composed of a mixture of three components - - as a R32/R134a/R600 mixed refrigerant.

Figure 3 is a triangular coordinate diagram showing an equilibrium state of a mixed refrigerant composed of a mixture of three components - - as a R125/R134a/R600 mixed refrigerant.

Figure 4 is a triangular coordinate diagram showing an equilibrium state of a mixed refrigerant composed of a mixture of three components - - as a R125/R134a/R600a mixed refrigerant.

Figure 5 is an illustrative diagram showing the method for filling a ternary mixed refrigerant consisting of the present invention.

### Explanation of symbols:

- 11 High-boiling-point refrigerant container
- 12 Measurer [measuring device] for a refrigerant with a high boiling point
- 13 Azeotrope-like mixture refrigerant container
- 14 Measurer for an azeotrope-like mixture refrigerant
- 15. Vacuum device
- 16 Refrigerant filling port
- 17 Pipe system
- 20 Refrigeration cycle apparatus
- 1V Saturated gas line of gas-liquid equilibrium line 1 corresponding to 50°C of R22
- 1L Saturated liquid line of gas-liquid equilibrium line 1 corresponding to 50°C of R22
- 2V Saturated gas line of gas-liquid equilibrium line 1 corresponding to 0°C of R22
- 2L Saturated liquid line of gas-liquid equilibrium line 1 corresponding to 0°C of R22
- 3V Saturated gas line of gas-liquid equilibrium line 1 corresponding to -50°C of R22
- 3L Saturated liquid line of gas-liquid equilibrium line 1 corresponding to -50°C of R22

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Figure 1

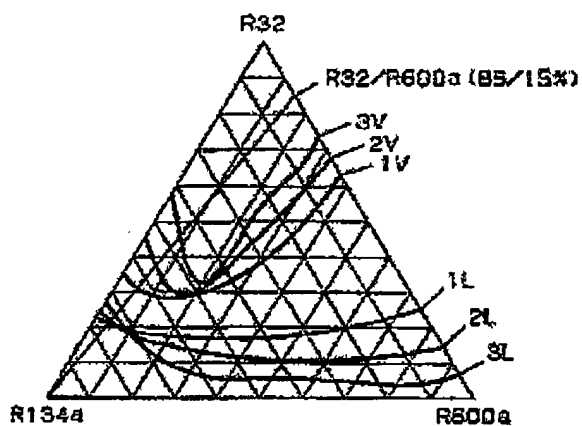


Figure 2

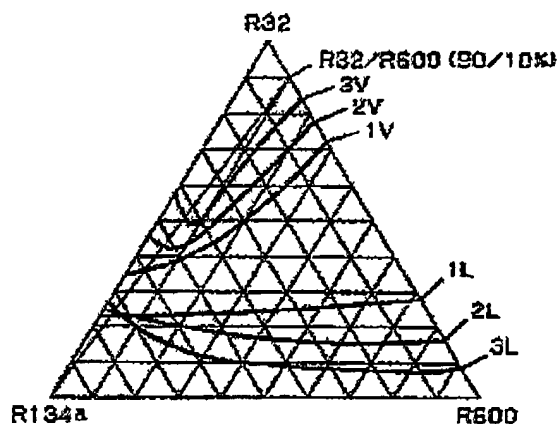


Figure 3

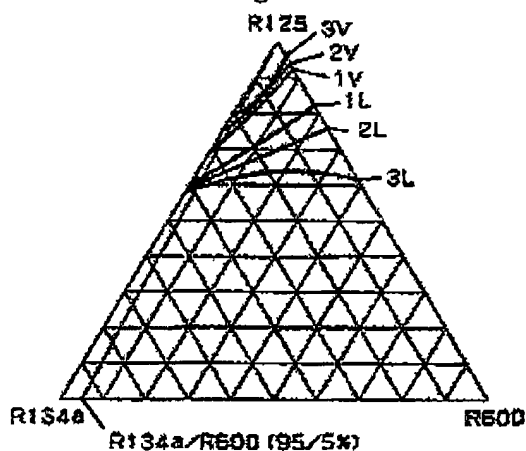


Figure 4

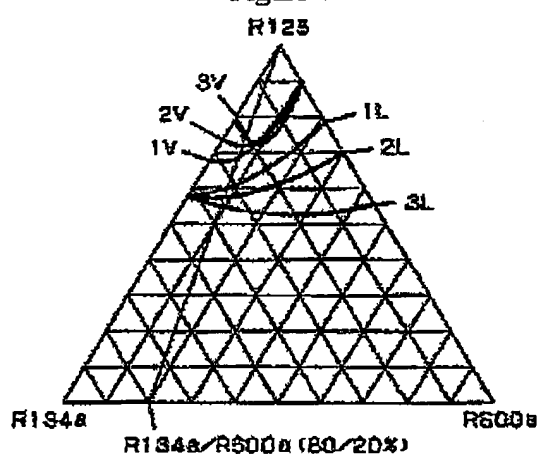
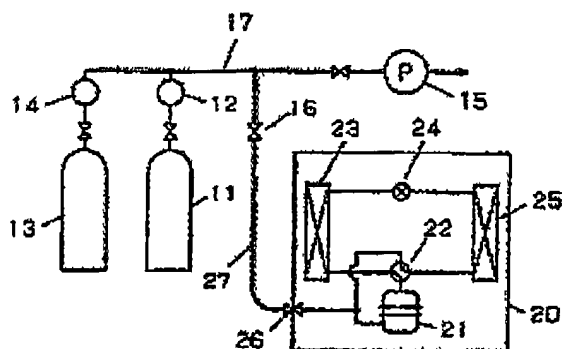


Figure 5:

- 11 High-boiling-point refrigerant container
- 12 Measurer for a refrigerant with a high boiling point
- 13 Azeotrope-like mixture refrigerant container
- 14 Measurer for an azeotrope-like mixture refrigerant
- 15. Vacuum device
- 16 Refrigerant filling port
- 17 Pipe system
- 20 Refrigeration cycle apparatus

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